

## IMPACT OF SPECIATION ON FLUORIDE, ARSENIC AND MAGNESIUM RETENTION BY NANOFILTRATION/REVERSE OSMOSIS IN REMOTE AUSTRALIAN COMMUNITIES

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**Abstract:** In order to provide safe drinking water in isolated communities where water supply and electrical infrastructure is limited, a system combining solar energy and advanced water treatment technology (a two-staged membrane process with ultrafiltration followed by nanofiltration/reverse osmosis) has been developed. The objective of this study is to model the speciation of commonly occurring and sometimes health-threatening trace contaminants, and then to evaluate the impact of speciation on fluoride, arsenic, and magnesium retention by nanofiltration/reverse osmosis. A series of experiments were performed in central Australia in late 2005 to assess elemental retention with four different membrane modules (BW30, ESPA4, NF90, and TFC-S) at various pH values between 3 and 11 at two different source waters (Pine Hill Station and Ti Tree Farm). The removal of fluoride and arsenic was observed to be independent of pH, while magnesium removal is pH dependent. Compound speciation is considered to explain dependence observations. Membrane type was found to impact retention. The results obtained in this study will provide valuable information on the reliability and the optimization windows of the renewable energy powered desalination system that has been developed.

**Keywords:** Nanofiltration, reverse osmosis, ultrafiltration, inorganic trace contaminant removal, speciation, photovoltaics

### Introduction

Water availability and quality in remote communities is a globally critical issue impacting human health. Improving access to clean drinking water is integrally linked to achieving all of the Millennium Development Goals [1]. Oftentimes, electrical infrastructure is also limited in remote areas, furthering the challenge of providing safe drinking water since most advanced water treatment technologies require energy. In order to address these issues, a renewable energy powered advanced water treatment system utilizing a two-staged membrane process - ultrafiltration (UF) followed by nanofiltration/reverse osmosis (NF/RO) - has been developed and tested in remote Australian locations [2, 3].

The presence of potentially health-threatening trace contaminants is an important concern with remote drinking water supplies. Many naturally-occurring compounds can be present in groundwaters and some are known to have significant health impacts [4-6]. For example, millions of people worldwide are at risk of acute chronic arsenic poisoning due to arsenic naturally found in groundwater [7, 8]. Well-known high arsenic groundwater areas include Argentina, Chile, Mexico, China, Hungary, West Bengal, Bangladesh and Vietnam – with more than 40 million people drinking water containing excessive arsenic concentrations in the Bengal Basin alone [9]. In Ghana, concentrations of iron, manganese, arsenic, fluoride, lead and chromium all have been found to exceed the World Health Organisation drinking water guidelines [10]. These contaminants may be naturally present in the groundwater, or may be caused by land-use and industry. Most notably, Ghana has a long history of gold mining. An undesired consequence of the mining is the contamination resulting from the release

of contaminants such as arsenic and mercury into both water and air in the surrounding and downstream areas [8, 11]. Other compounds present in natural waters may not have known negative health impacts, but rather have aesthetic consequences that make the water less desirable for consumption [4-6]. In order for remote drinking water supplies to be most beneficial to communities, it is important that the water is desirable from both health and aesthetic perspectives.

Water quality characteristics, such as pH, are very important when considering the presence of inorganic trace contaminants. Smedley and Kinniburgh [9] found that there are two main triggers that lead to the release of arsenic on a large scale. First is the development of high pH conditions (>8.5) in semi arid or arid environments which leads to the desorption of adsorbed arsenic and the second is the development of strongly reducing conditions at near-neutral pH values again resulting in the desorption of arsenic [9]. Typical pH values of groundwaters vary significantly globally, and thus an understanding of how inorganic trace contaminants behave at varying pH levels via speciation modelling is important.

This paper will discuss the speciation of many commonly occurring inorganic trace contaminants, and then relate speciation observations to retention results using NF/RO for fluoride, arsenic, and magnesium. Fluoride can lead to dental and skeletal fluorosis and the drinking water guideline is 1.5 mg/L [4]. Typical concentrations of fluoride in groundwaters usually do not exceed 10 mg/L [4]. Arsenic, with a drinking water guideline of 0.01 mg/L, can lead to skin damage and circulatory problems, and is a potential carcinogen [4, 6]. A large range of arsenic concentrations can be found in natural waters, from  $< 5 \cdot 10^{-4}$  to  $> 5$  mg/L [9]. There is no drinking water guideline for magnesium, whose concentrations in groundwater vary greatly, although high concentrations of magnesium can result in unpleasant taste [4].

NF/RO membranes are well-accepted water treatment technologies capable of desalination and reducing concentrations of other compounds found in natural waters. NF removes multivalent ions and has high organics removal, while RO retains both mono- and multivalent ions. NF/RO membranes are hydrophilic, typically negatively-charged polymers, and removal of ions tends to be specific to the particular membrane and ion characteristics and speciation [12]. NF/RO membranes can be effective at reducing nitrate, arsenic, aluminium, fluoride, and uranium concentrations in natural waters [13].

A study was completed to evaluate the effect of pH on the removal of commonly-occurring groundwater compounds using NF/RO membranes in remote Australian communities. This paper will discuss the speciation of common groundwater compounds and then focus on assessing the impact of speciation on retention of selected compounds of this study, namely fluoride, arsenic and magnesium with NF/RO.

### Methods and Materials

The photovoltaic-powered reverse osmosis desalination system (PV-membrane) is a two-staged membrane system and details were published elsewhere [2]. In order to specifically assess the effect of pH on trace contaminant removal, a series of experiments were performed by adjusting the pH and subsequently evaluating compound retention with four different membrane modules (BW30, ESPA4, NF90, and TFC-S) at two different source waters in Australia (Pine Hill Station and Ti Tree Farm) [14].

At Pine Hill Station, each of the four membrane modules was tested, while BW30 was also tested at Ti Tree Farm. During each experiment, pH values of the bore water were adjusted in increasing step-wise increments between 3 and 11 with hydrochloric acid and sodium hydroxide. Once equilibrated (typically within 30-60 minutes), samples were collected from feed, UF permeate, NF/RO permeate, and concentrate streams and performance readings were measured. NF/RO permeate and concentrate were re-circulated into the feed tank. All experiments were conducted while the PV-membrane system was operating with a constant power source to ensure that pH was the only variable.

The samples were then analysed for the concentration of commonly-occurring groundwater compounds, including common salts, heavy metals, and health-threatening trace contaminants. Prior to analysis, samples were acidified with nitric acid (~1% v/v). Cation analysis was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma atomic mass spectroscopy (ICP-MS), and anion analysis by ion chromatography (IC) (Dionex AS18) by the Australian Nuclear Science and Technology Organisation (ANSTO, Australia).

Speciation modelling was conducted using the Visual MINTEQ (version 2.53) software package. Source water parameters were entered according to compound concentrations determined experimentally at Pine Hill Station, and a "sweep test" was run based on component activity to evaluate the speciation of the predominant forms of each compound between the pH range of 3 to 11 in steps of 0.5. Several assumptions were made to conduct speciation modelling, including a fixed carbonate concentration (at a partial pressure of  $3.8 \cdot 10^{-4}$  atm) and temperature of 25°C. Valence states of components were also assumed based on general groundwater information and phase diagrams and it was ensured that the charge difference between cations and anions remained  $\leq 5\%$ .

Figure 1 shows the field testing of the PV-membrane system when these experiments were conducted.

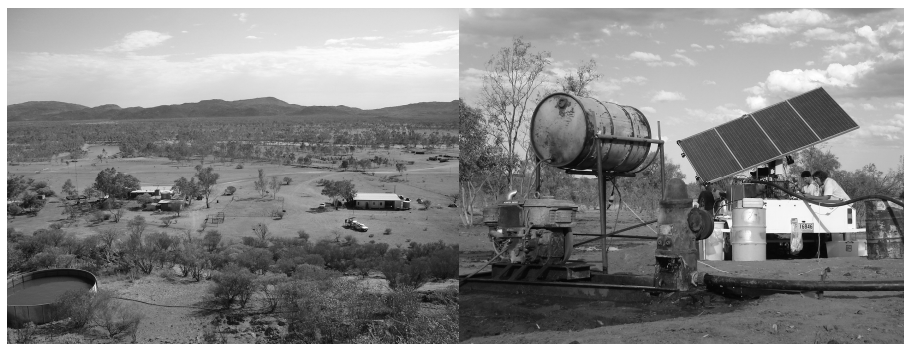


Figure 1. Field testing of PV-membrane system at Pine Hill Station, Northern Territory, Australia: (A) aerial overview of Pine Hill Station and (B) system operation at the borewater pump outlet

## Results and Discussion

Speciation models can assist in explaining how the solubility of particular compounds can impact retention. Figure 2 shows the predicted speciation of fifteen commonly occurring groundwater compounds at Pine Hill by presenting the percentage of relative species of each compound as a function of pH. Several trends can be observed from analyzing these diagrams. Calcium, magnesium, manganese, nickel, and strontium all have major changes to primarily aqueous carbonate salt species at high pH values. Vanadium and zinc also convert nearly completely to carbonate salt species at high pH values, but first go through an intermediate transition stage. Arsenic, fluoride, potassium, and sodium all exhibit one significant switch in primary species at a pH which corresponds to the chemical properties of the compound (i.e. acid dissociation constant). While the speciation of some compounds such as molybdenum and phosphate is quite complicated, the speciation of other compounds is not significantly impacted by pH. Chloride speciation is shown as a representative example for chloride, copper, nitrate, selenium, and sulphur, all of which demonstrate this pH independence of speciation.

This study focuses on the impact of fluoride, arsenic, and magnesium speciation on retention by nanofiltration/reverse osmosis, so a more in-depth discussion of the speciation and retention of these

compounds is warranted. Fluoride is primarily present as  $F^-$  above pH 3 and there are no major species changes between pH 3 and 11. Since this is the range that was studied experimentally, it is expected that there is no apparent pH dependence of retention observed experimentally. Similarly, arsenic transitions at approximately pH 7 from being primarily  $HAsO_4^{2-}$  to primarily  $H_2AsO_4^-$ . Since both of these compounds are arsenate ( $As^{5+}$ ) based rather than arsenite ( $As^{3+}$ ) based, this change in species should not impact retention because arsenate retention has previously been observed to be independent of pH even though the removal of arsenite ( $As^{3+}$ ) is impacted by pH [15]. The magnesium speciation shows that a major change in species occurs between pH 9 and 10. At pH values above this transition point, nearly all of the magnesium present is  $MgCO_3(aq)$  which could precipitate out of solution if concentrations near the boundary layer exceed the solubility limit. This effect would impact retention, especially if precipitation occurs and magnesium remains on the membrane surface.

Figure 3 shows the concentrations of fluoride, arsenic, and magnesium in the feed, UF permeate, NF/RO permeate, and concentrate streams when the experiment was run at Pine Hill using a NF90 membrane module. Salt retention ( $MgSO_4$ ) of the NF90 membrane, as reported by the manufacturer, is 95% under the following test conditions: 2000 ppm  $MgSO_4$ , 4.8 bar, 25°C, and 15% recovery [2]. Fluoride was consistently retained by the membrane at pH values between 3 and 11, as expected, with concentrations in the permeate near or below the drinking water guideline. Average removal of fluoride was  $\geq 88\%$ . Similarly, arsenic removal is independent of pH as expected and concentrations in all streams were below the drinking water guideline. The average retention of arsenic is 78%. Magnesium also is highly retained by NF90, with an average retention of 99%. However, unlike arsenic and fluoride, the removal of magnesium demonstrates dependence on pH due to its speciation. The concentrations of magnesium in each stream drop dramatically above pH 9 indicating precipitation occurs at high pH and that the magnesium may be accumulating on the membrane surface as a precipitate ( $MgCO_3$ ). Magnesium serves as an example to demonstrate that the impact of pH on retention is significant with certain compounds due to the solubility of the species at different pH values. Due to the principles of membrane separation, concentrations in the feed are expected to be the same as in the UF permeate because UF membranes do not typically remove ions [12]. An indication of minor analytical error is shown in the occasional case that concentrations in the UF permeate are slightly higher than feed concentrations.

Such analysis is important because it can help determine the optimal operating range for the PV-membrane system. As demonstrated by magnesium, precipitating compounds impact retention, which can result in membrane fouling and scaling, decreasing the performance of the system. Flux across the membrane decreased slightly from  $24.2 \text{ L/(h}\cdot\text{m}^2)$  to  $22.5 \text{ L/(h}\cdot\text{m}^2)$  during the course of the experiment which could be attributed to precipitation on the membrane surface.

These experiments also assessed the impact of membrane type and source water on compound retention. Membrane type was also observed to impact compound retention. Average retention of arsenic was 79%, 65%, and 75% for the BW30, TFC-S, and ESPA4 membranes, respectively. Magnesium retention was 99%, 96%, and 92% for the same respective membranes. Variations in retention based on membrane type are likely due to membrane characteristics. Experiments with BW30 were repeated with a secondary groundwater at Ti Tree Farm. Retention and pH dependence observations were similar at Pine Hill and Ti Tree Farm. Extensive retention and system performance results are in preparation for publication in the Environmental Science and Technology series (or similar) [2].

## Conclusions

The objective of this study was to determine the speciation of an Australian groundwater and evaluate the possible impact of pH variations on retention by NF/RO. Speciation assists in predicting the dissociation and precipitation of certain species. Fluoride, arsenic, and magnesium were the focus of this study, and it was shown how the speciation of these compounds affects their retention by NF/RO.

Results showed the removal of fluoride and arsenic to be independent of pH and magnesium removal to be pH dependent, which corresponds to speciation trends. These results have important significance in many parts of the world, as the pH of natural waters varies greatly and fluoride, arsenic,

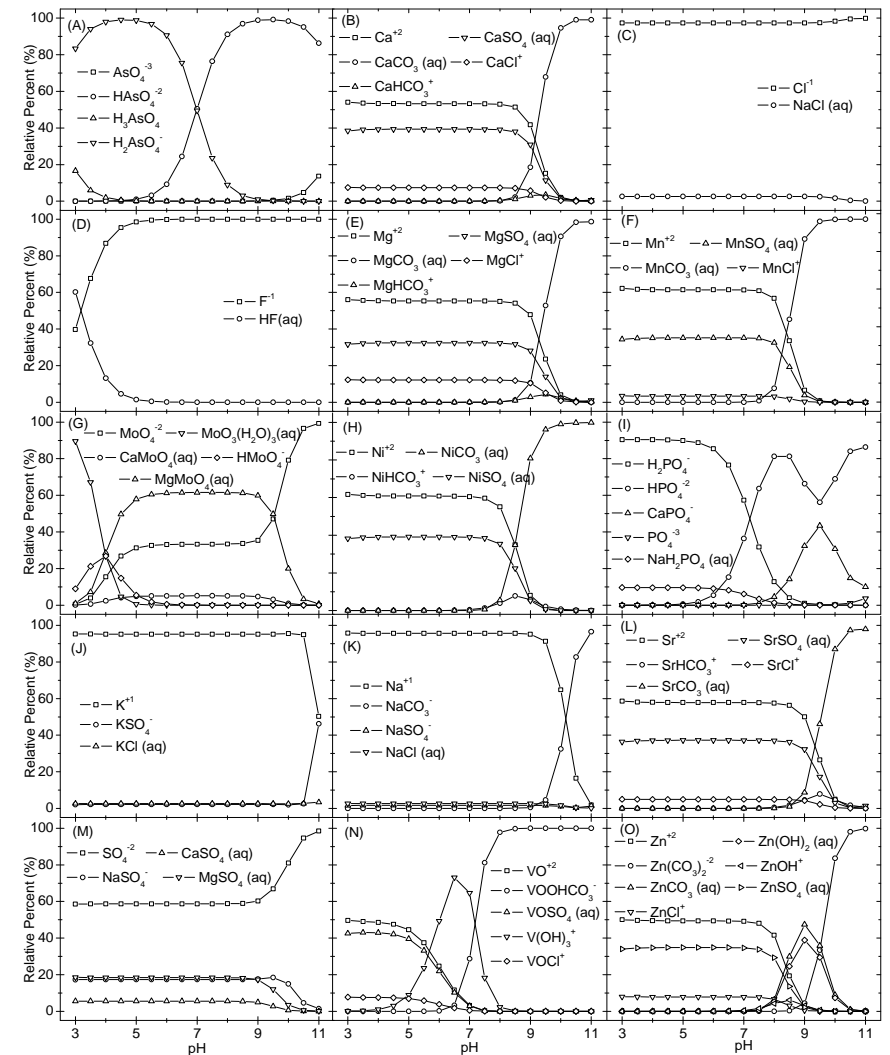


Figure 2. Predicted Speciation of Selected Groundwater Compounds at Pine Hill: (A) Arsenic; (B) Calcium; (C) Chloride; (D) Fluoride; (E) Magnesium; (F) Manganese; (G) Molybdenum; (H) Nickel; (I) Phosphate; (J) Potassium; (K) Sodium; (L) Strontium; (M) Sulphate; (N) Vanadium; (O) Zinc

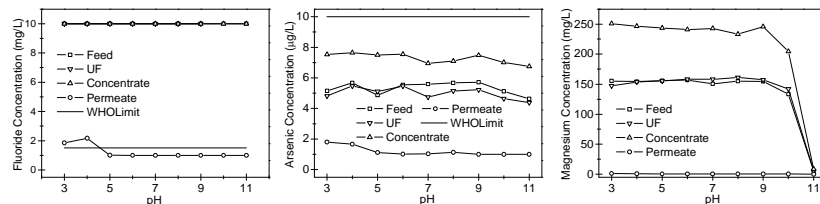


Figure 3. Concentration of fluoride, arsenic, and magnesium in feed, UF permeate, NF/RO permeate, and concentrate as a function of pH for NF90 at Pine Hill compared to the World Health Organisation guideline value

and magnesium are commonly occurring groundwater contaminants. Evaluating the impact of speciation on NF/RO performance leads to improved understanding of both the limitations and value of using a system combining renewable energy and advanced water treatment technology in many parts of the world.

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